

IMPROVED PROCESSES OF HYDROGEN PEROXIDE PREPARATION

Field of the Invention

The present invention relates to simplified processes for the preparation of hydrogen peroxide (H_2O_2). H_2O_2 is a known oxidizer and disinfectant that is used in many industrial processes having many uses in the pharmaceutical, electronic, food and water purification industries.

Currently, H_2O_2 is only manufactured in a chemical manufacturing industrial environment and shipped to the end-user. The current manufacturing process is the Anthraquinone Process (AP) producing H_2O_2 from 2-ethyl anthraquinone. This is a two stage process; wherein the first stage 2-ethyl anthraquinone reacts with Hydrogen (H_2) over a lead catalyst to produce 2-ethyl dihydroanthraquinone and in the second stage, the 2-ethyl dihydroanthraquinone, from the first stage, reacts with O_2 to produce H_2O_2 and 2-ethyl anthraquinone for recycle. This process requires the handling of two explosive chemicals, H_2 and O_2 , as well as the handling of hazardous anthraquinone chemistries. AP requires an industrial manufacturing environment for the production of H_2O_2 due to the safety issues associated with: the chemicals, the manufacturing process and the handling/transportation of H_2O_2 .

The present invention presents the use of sulfuric acid (H_2SO_4) as a catalyst utilizing water and electricity as the only raw materials for the production of H_2O_2 . The present invention utilizes membrane technology in combination with electrolysis to produce H_2O_2 at the site of the end-user, whereupon H_2O_2 can immediately be utilized. The present invention eliminates the need for transportation and storage of H_2O_2 .

H_2O_2 is an ideal oxidizer and disinfectant in water purification systems, especially drinking water purification. All other disinfectants create disinfection by-products upon their reaction with Natural Organic Matter (NOM) in the water. Many disinfection by-products currently produced from chlorine, chlorine dioxide and ozone are known toxins, carcinogens and teratogens in drinking water. In contrast, other than the oxidized organic molecule, H_2O_2 after reaction breaks down to water (H_2O) and Oxygen (O_2).

H_2O_2 has significant uses in the electronics industry in the manufacture of miniature circuitry. In these applications, the purity of H_2O_2 is critical to the manufacture of circuits which will not short or open. In this invention, many processes and materials are eliminated in the manufacture of H_2O_2 , thereby allowing for the production of a purer product.

Background of the Invention and Description of the Prior Art

In the nineteenth century, H_2O_2 was produced exclusively on a commercial scale by the reaction of an acid upon barium peroxide, which is readily formed by heating barium oxide in air. The barium oxide was then usually reacted with sulfuric acid to produce H_2O_2 along with a solid precipitate of barium sulfate. H_2O_2 is normally produced in the laboratory by the reaction of sodium peroxide with water or dilute hydrochloric acid. In this reaction sodium oxide reacts with either H_2O or hydrochloric acid to form H_2O_2 along with either sodium hydroxide, in the case of H_2O , or sodium chloride, in the case of hydrochloric acid.

Until the mid 20'th century, H_2O_2 was produced by the electrolysis of H_2SO_4 , the Sulfuric Acid Process (SAP). SAP is a two stage process wherein the first stage H_2SO_4 is electrochemically converted to $H_2S_2O_8$ and H_2 . In the second stage, the $H_2S_2O_8$ from the first stage is reacted with H_2O to form H_2O_2 and H_2SO_4 for recycle. At that time, this process was not

as economical or as safe to operate as AP. At that time, SAP required the energy of electrolysis along with two stages of distillation, wherein the first stage of distillation required the separation of an explosive chemical, H₂, and the second stage of distillation required the separation of H₂O₂ from very corrosive H₂SO₄. AP replaced SAP due to both economical and safety issues.

5 However, AP presents other issues, the first of which is safety. AP requires an industrial manufacturing environment. H₂O₂ is a very hazardous chemical to store and to transport. Once produced, H₂O₂ requires specialized equipment in storage and in transportation. H₂O₂ at concentrations of over approximately 20% can react violently with organic materials and with acids. H₂O₂ in concentrations of over 50% can explosively decompose or react with any electron 10 acceptor material, such as acids, or organic materials. Another issue in relation to AP production of H₂O₂ is purity. The AP process is rather complex. The steps in this process to produce high purity H₂O₂ include: hydrogenation, oxidation, extraction, solvent scrubbing, settling, cation resin treatment, carbon treatment, cation resin treatment, distillation, absorption and dilution. The product after initial cation resin treatment is a very pure product except for the presence of 15 various organic species, which is one of the critical contaminants in all drinking water purification, pharmaceutical and electronics applications, namely, total carbon.

Perhaps the most significant application problem with H₂O₂ is in the electronics industry, wherein at the present time, contamination is a critical issue during the manufacture of microcircuit devices. As these devices become more complex, and smaller in dimension, 20 production sensitivity to the presence of contaminants becomes more of a problem. Contaminants in the form of solid particles, can open or short a circuit, affect photolithographic reproduction, alter electrical properties and even damage the crystal structure of these electronic devices.

In addition to the electronics industry, there are many uses for H₂O₂ in the water purification industry. Oxidation and disinfection processes with H₂O₂ produce much purer products than processes with other oxidizers. Chlorine, chlorine dioxide, ozone, chloramines and bromine all produce by-products of disinfection that are either: toxic, carcinogenic or teratogenic. As such, these by-products are health issues to humanity, plant and animal life. In contrast, the products of oxidation with H₂O₂ are usually limited to O₂ and H₂O, along with the product of oxidation. However, most water purification facilities are not interested in the storage and handling of H₂O₂ due to the safety issues associated with H₂O₂.

This instant invention proposes end-use on-site production of H₂O₂ utilizing SAP instead of AP. This instant invention presents an improvement upon SAP by performing separation with membranes instead of by distillation. The utilization of membranes, either inorganic or organic or a combination thereof would provide the ability of on-site production of H₂O₂ utilizing SAP, thereby eliminating the need for AP, as well as the transportation, storage and handling of H₂O₂.

Membrane technologies have been available since the early 1990's. Early versions of this technology were of organic form only. As of late, inorganic materials have been incorporated in many applications. As of late, membrane technologies have been improved to incorporate electrolysis directly onto the membrane. This is accomplished by various methods, which make the membrane conductive; this conductivity can be accomplished in both inorganic and organic membranes.

In fuel cells, U.S. Pat. No. 4,490,445 teaches a solid oxide electrochemical energy converter comprising of alternate layers of solid oxide electrolyte plates and electrical conductor plates. Each electrolyte plate includes a coating of a porous oxidizer electrode on a first surface of the electrolyte and a coating of a porous fuel electrode on a second surface of the electrolyte.

Each conductor plate includes grooved networks formed by ridges which define gas passages on both surfaces of the conductor plate, such ridges being in electrical contact with the electrode coatings on next adjacent electrolytes. Each conductor plate also possesses a means for tapping electricity from or introducing electricity into the converter. The conductor plates also possess 5 circumferential ridges arranged along the edges of the conductor plate to define gas seals, the ridges being in contact with surface coatings on next adjacent electrolyte plates, which surface coatings possess the same composition as that of the electrode coatings.

U.S. Pat. No. 4,791,079 discloses two-layer conducting catalytic ceramic membranes which are suitable for use in a variety of hydrocarbon conversion reactions. The two-layer 10 membrane possess one layer formed of an impervious mixed ion and electronic conducting ceramic such as yttria stabilized zirconia which is doped with sufficient CeO₂ or TiO₂ to impart electron conducting characteristics to the ceramic. A second layer associated with mixed conducting impervious ceramic is a porous ion conducting layer containing a selective hydrocarbon oxidation catalyst.

15 A variety of methods have been presented for the separation of oxygen form air. A solid electrolyte oxygen pump formed from a plurality of solid-state membranes is presented in U.S. Pat. No. 4,877,506. The oxygen pump possesses electrodes which form a plurality of linear, parallel channels on facing surfaces of the electrolyte. The air feed is introduced into the channels formed of the air electrode. Oxygen formed during operation of the device is removed 20 by passage through the electrolyte via channels formed of the oxygen electrode or anode. A monolithic array is formed by situating an interconnecting material between adjacent cells to form a stack of cells. U.S. Pat. No. 5,034,023 discloses ceramic honeycomb structures which are capable of separating oxygen from an oxygen-containing gaseous mixture. The channeled

honeycombs are formed from a solid electrolyte having at least some of the honeycomb channels sealed at one of its faces. The oxygen-containing gas is introduced into a first set of channels at one face of the honeycomb, a first voltage is applied to the interior walls of the channels and a second voltage is applied to the interior walls of the second set of remaining channels thereby

5 creating an electrical potential across the ceramic material separating adjacent channels of the two sets. The electrical potential drives oxygen ions through the channel walls releasing molecular oxygen into the second set of channels which can be collected. U.S. Pat. No. 5,045,169 discloses an electrochemical device capable of generating oxygen from air upon the application of an electrical current, where a plurality of adjacent electrochemical cells are

10 electrically connected in series, each cell containing an inner, porous oxygen electrode; a dense, solid oxide electrolyte capable of transporting oxygen ions partly disposed on top of the inner electrode and partly disposed between inner electrodes of adjacent cells; an outer porous air electrode disposed on top of the electrolyte; and separate, dense, electronically conductive segments of interconnection material disposed between adjacent cells, the interconnection

15 electrically and physically connecting the outer air electrode from one cell to the inner oxygen electrode from an adjacent cell, the device having gas impermeable, dense, contacting segments of electrolyte and interconnection material between the inner electrode of adjacent cells. U.S. Pat. No. 5,240,480 discloses representative solid-state membranes for separating oxygen from oxygen-containing gaseous mixtures. These membranes comprise a multi-component

20 metallic oxide porous layer having an average pore radius of less than about 10 micrometers and a multi-component metallic oxide dense layer having no connected through porosity wherein the porous layers and dense layers are contiguous and such layers conduct electrons and oxygen ions at operating temperatures.

U.S. Pat. No. 5,356,728 and European Patent Application WO 94/24065 disclose cross-flow electrochemical reactor cells formed from multi-component metallic oxides of the perovskite structure which demonstrate electron conductivity and oxygen ion conductivity at elevated temperatures. Such cells are useful in carrying out partial oxidation reactions of organic compounds to form added-value products and separating oxygen from oxygen-containing gaseous mixtures. The cross-flow reactor cells of U.S. Pat. No. 5,356,728 comprise either a hollow ceramic blade positioned across a gas stream flow containing one or more channels for flow of gas streams or a stack of crossed hollow ceramic blades containing one or more channels for flow of gas streams. Each channel has at least one channel wall disposed between a channel and a portion of an outer surface of the ceramic blade or a common wall with adjacent blades in a stack comprising a gas impervious multi-component metallic oxide, typically of a perovskite structure, which exhibits electron conductivity and oxygen ion conductivity at elevated temperatures. Thus, the channels are contiguous to the outer surface of the ceramic blade which is formed from the multi-component metallic oxide.

None of these patents teach or suggest electrolysis and membrane separation or electrolytic membrane separation as methods of H₂O₂ preparation.

In H₂O₂ manufacturing, membranes have been discussed as methods of H₂O₂ purification. U.S. Patent Nos. 4,879,043 and 6,333,018 present the use of reverse osmosis membrane technology as a final purification step in the production of H₂O₂ manufactured by AP. U.S. Patent Nos. 5,215,665; 5,262,058 and 5,906,738 present the use of reverse osmosis membrane technology in combination with cationic resin technology as final purification steps in the production of H₂O₂ manufactured by AP. U.S. Patent Nos. 5,851,042 and 6,113,798 present the use of converting contaminant particles by reacting said particles with micro-ligands, then

separating said reaction products with membranes as a final purification step in the production of H₂O₂ manufactured by AP. None of these patents teach or suggest electrolysis and membrane separation or electrolytic membrane separation as methods of H₂O₂ preparation.

U.S. Patent No. 5,800,796 presents an electrochemical reactor wherein O₂ and H₂ are reacted across a conductive membrane containing reducing catalysts forming H₂O₂. This novel process eliminates AP while simplifying the process of H₂O₂ production. However, the potential for contamination of H₂O₂ with heavy metals from the reducing catalysts is significant. Heavy metals contamination eliminates the potential use of H₂O₂ in either the production of micro-circuitry or water purification. In addition, the potential safety issues from the reaction of very explosive O₂ and H₂ in an electrolytic environment preclude the potential use of this process at the end-use site.

All of these applications and many other industry applications of organic and inorganic membranes have shown the potentiality of membrane technologies. However, none of these applications or any other industrial application has proposed the use of membranes to improve the manufacturing process or the safety associated with and/or the handling of H₂O₂.

Summary of the Invention

A primary object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂.

Another object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂, wherein the safety in handling of H₂O₂ is improved.

Another object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂, wherein significant storage of concentrated H₂O₂ is not required.

Another object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂, wherein transportation of H₂O₂ is not required.

Another object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂, wherein a higher purity H₂O₂ is manufactured.

5 Another object of the invention is to devise an effective, efficient and economically feasible process for producing H₂O₂ utilizing H₂SO₄ as a catalyst along with water and electricity as the raw materials.

10 Another object of the invention is to devise an effective, efficient and economically feasible process for handling H₂O₂ at water treatment plants so that hydrogen peroxide is an attractive alternate to other oxidizers and disinfectants utilized at water treatment plants.

Description of the Preferred Embodiments

This invention simplifies the manufacture of H₂O₂, eliminates the need to store large volumes of concentrated H₂O₂ and eliminates the need to transport concentrated H₂O₂. The 15 present invention presents the use of sulfuric acid (H₂SO₄) as a catalyst utilizing water and electricity as the only raw materials for the production of H₂O₂. The present invention utilizes membrane technology in combination with electrolysis to produce H₂O₂ at the site of the end-user, whereupon H₂O₂ can immediately be utilized. The Sulfuric Acid Process (SAP) is presented as a two stage process wherein the first stage H₂SO₄ is electrochemically converted to 20 H₂S₂O₈ and H₂. The H₂ is separated and potentially used in a fuel cell to produce electricity. In the second stage, the H₂S₂O₈ from the first stage is reacted with H₂O to form H₂O₂ and H₂SO₄. H₂SO₄ is optionally recycled for electrochemical conversion, again, to H₂S₂O₈ and H₂. Since it can be very cost ineffective to perform separations which are precisely complete, separation in this invention is to be defined to mean substantial separation or separation of such percentage 25 that the chemical process and the application of H₂O₂ in the final application performs as indented. It is to be understood that within a stage of separation, whether that separation be of

distillation or of membrane technology, that improved separation can be accomplished with multiple stages of separation as compared to a single stage.

In this invention it is most preferred to produce H₂O₂ in a two stage process, wherein the first stage H₂SO₄ is electrolytically converted into H₂S₂O₈ and H₂, and wherein the second stage 5 H₂S₂O₈ is reacted with H₂O to produce H₂O₂ and H₂SO₄. It is a preferred embodiment of this invention to utilize at least a portion of the H₂ produced in the first stage in a fuel cell to generate electricity. It is a preferred embodiment of this invention to use at least a portion of the electricity generated from the H₂ fuel cell to electrolytically convert H₂SO₄ into H₂ and H₂S₂O₈.

It is preferred that the electrolysis in the first stage be performed on at least one of an 10 organic and an inorganic membrane that is electrically conductive. Membrane conductivity can be accomplished by any means known in the art. It is preferred to perform electrolysis in the first stage and that the separation of H₂ from H₂S₂O₈ is performed by at least one of membrane separation and distillation. It is most preferred to perform electrode electrolysis in the first stage with electrode(s) made of material(s) which are corrosion resistant. Corrosion resistant electrode 15 materials are preferably at least one of: zirconium, hastelloy and titanium. It is most preferred that the separation of H₂ from H₂S₂O₈ be performed with a membrane. It is preferred that the separation of H₂ from H₂S₂O₈ be performed with distillation.

It is most preferred that, in the second stage, the separation of at least one of H₂O₂ and 20 any unreacted H₂O from at least one of H₂S₂O₈ and H₂SO₄ be performed with membranes. It is most preferred that the separation of H₂SO₄ from H₂S₂O₈ in the second stage be performed with membranes. It is an embodiment that the separation of at least one of H₂O₂ and any unreacted H₂O in the second stage from at least one of H₂S₂O₈ and H₂SO₄ be performed with distillation. It is an embodiment that the separation of H₂SO₄ from H₂S₂O₈ in the second stage be performed

with distillation. It is most preferred that the second stage be separated into two portions, wherein at least one of H₂O₂ and H₂O are separated from at least one of H₂S₂O₈ and H₂SO₄ in the first portion and H₂SO₄ is separated from H₂S₂O₈ in the second portion. It is most preferred that the separated H₂SO₄ in the second stage be recycled to the first stage.

5 It is most preferred that an excess amount of H₂O be added to the second stage so that the produced H₂O₂ is dilute upon formation to a concentration which maximizes safety in a given end-use application. It is preferred that the H₂O₂ produced in the second stage be diluted with H₂O, upon separation of the H₂O₂ from at least one of H₂SO₄ and H₂S₂O₈, to a concentration which maximizes safety in a given end-use application.

10 It is most preferred that the production of H₂O₂ by the processes in this invention be performed at the end-use location so as to minimize or eliminate vehicular transportation of H₂O₂. It is most preferred to utilize H₂O₂ manufactured by the processes of this invention in the manufacture of electric circuit devices. It is most preferred to utilize H₂O₂ manufactured by the processes of this invention in the purification of water.

15 Certain objects are set forth above and made apparent from the foregoing description. However, since certain changes may be made in the above description without departing from the scope of the invention, it is intended that all matters contained in the foregoing description shall be interpreted as illustrative only of the principles of the invention and not in a limiting sense. With respect to the above description, it is to be realized that any descriptions, drawings and examples deemed readily apparent and obvious to one skilled in the art and all equivalent relationships to those described in the specification are intended to be encompassed by the present invention.

20 Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention. It is also to be understood that the following claims are

intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which, as a matter of language, might be said to fall in between.

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I claim:

1. A process for the preparation of H₂O₂ wherein,

H₂O₂ is produced by first electrolysis converting H₂SO₄ into H₂ and H₂S₂O₈ and then second by reacting the H₂S₂O₈ formed in the first reaction with H₂O in a second reaction to

5 form H₂O₂ and H₂S₂O₈ and wherein,

at least one of the separation of H₂ from H₂S₂O₈ and the separation of H₂O₂ from H₂SO₄ is performed with a membrane.

2. The process according to claim 1, wherein the membrane is constructed of organic materials.

10 3. The process according to claim 1, wherein the membrane is constructed of inorganic materials.

4. The process according to claim 1, wherein the H₂SO₄ is recycled from the second reaction to the first reaction.

5. The process according to claim 1, wherein the membrane utilized to separate the

15 products of the first reaction separates H₂ from H₂SO₄.

6. The process according to claim 1, wherein the membrane utilized to separate the products of the second reaction separates H₂O₂ from H₂S₂O₈.

7. The process according to claim 1, wherein the membrane utilized to separate the products of the second reaction separates H₂O from at least one of H₂SO₄ and H₂S₂O₈.

20 8. The process according to claim 1, wherein the electrolysis in the first reaction is performed across an electrically charged conductive membrane.

9. The process according to claim 1, wherein the electrolysis in the first reaction is performed with metal electrodes.

10. The process according to claim 9, wherein the electrodes are made of at least one of: zirconium, hastelloy and titanium.

11. The process according to claim 1, wherein at least one of the separation processes is performed with distillation.

5 12. The process according to claim 11, wherein distillation separates H₂ from H₂SO₄.

13. The process according to claim 11, wherein distillation separates H₂O₂ from H₂S₂O₈.

14. The process according to claim 11, wherein distillation separates H₂O from at least one of H₂SO₄ and H₂S₂O₈.

10 15. The process according to claim 1, wherein the second reaction operates with an excess of H₂O forming an aqueous concentration of H₂O₂.

16. The process according to claim 1, wherein H₂O is added to the final H₂O₂ product from the second reaction forming an aqueous concentration of H₂O₂.

15 17. The process according to claim 1, wherein there is no vehicular transportation of H₂O₂.

18. The process according to claim 1, wherein the H₂ produced in the first reaction is utilized in a fuel cell to generate electricity.

19. The process according to claim 18, wherein at least a portion of the electricity generated in the fuel cell is used for the electrolytic conversion of H₂SO₄ into H₂ and H₂S₂O₈.